Synthetic Methods

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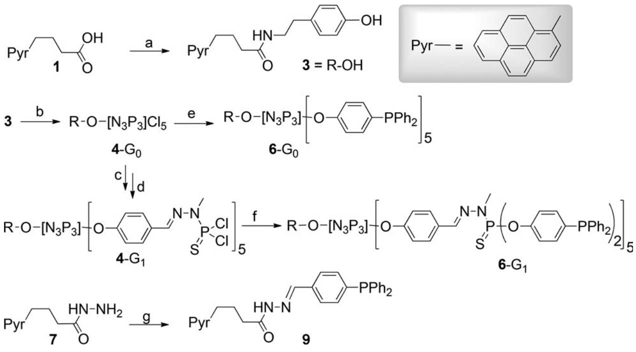
Pyrene-Tagged Dendritic Catalysts Noncovalently Grafted onto Magnetic Co/C Nanoparticles: An Efficient and Recyclable System for Drug Synthesis**

Michel Keller, Vincent Collière, Oliver Reiser, Anne-Marie Caminade, Jean-Pierre Majoral,* and Armelle Ouali**

The reuse of catalysts is highly desirable for economic and ecological reasons, and to this day constitutes an important challenge. Along these lines, magnetic nanoparticles (MNP) are increasingly recognized as appealing supports for catalytic systems in the development of more efficient and green processes.[1] Contrary to conventional supports, such as polymers or silica, which require time-consuming precipitation and filtration steps,[2] their separation can easily be achieved by magnetic decantation. Moreover, MNPs are mechanically robust and can be easily agitated during a reaction by application of an external magnetic field.[3] Generally, MNPs are stabilized by coating the magnetic core with polymer or silica shells, which are used for the covalent immobilization of homogeneous catalysts.[1] Magnetic carbon-coated nanoparticles[4] have also been used as reusable supports for the covalent immobilization of catalysts;[5] however, their graphene-like shell offers the unique possibility for non-covalent catalyst attachment by π–π stacking,[6] a concept that was recently demonstrated with pyrene-tagged[7] Pd monomeric complexes. Covalently immobilized dendronized catalysts, which possess an anchoring site and branches terminating with active sites, represent another promising strategy for recoverable catalysts, as they were shown to afford enhanced surface functionalization[8] and better catalytic activity than corresponding monomeric catalysts.[8a,d] Combining both strategies, we planned to graft pyrene-tagged dendritic Pd-phosphine catalysts onto Co/C MNPs by π–π stacking, and to evaluate the activity and recyclability of the resulting composites in Suzuki reactions.

Pyrene derivative **3** was prepared in high yield (91%) from commercial **1** and tyramine **2** (Scheme 1). **3** was allowed to react with $N_3P_3Cl_6$ and Cs_2CO_3 to afford **4**-G_0 in 81% yield. The growth of this dendron was achieved by using the reactivity of the P−Cl bonds towards phenolic group of 4-OH-C_6H_4-CHO (step c) and further condensation of the aldehydes with $H_2NNMeP(S)Cl_2$ to afford 1st generation dendron **4**-G_1 (step d). The Cl-terminated dendrons **4**-G_0 and **4**-G_1 were reacted with phosphine **5**[9a] to yield pyrene-tagged multivalent phosphines **6**-G_0 and **6**-G_1 (steps e and f). Incorporation of pyrene labels on the surface of dendrimers has been previously achieved, but **6**-G_0 and **6**-G_1 constitute the first examples of phosphorous dendrons with pyrene cores.[10] Moreover, the monomeric pyrene-tagged phosphine **9** was prepared by condensation between **7** and phosphine **8**.[9b]



Scheme 1. Synthesis of pyrene (Pyr)-tagged phosphines **6**-G_0, **6**-G_1, and **9**: a) H_2N-$(CH_2)_2$-C_6H_4-OH (**2**), DMF, EDC, HOBt, 0–20°C (91%); b) $N_3P_3Cl_6$ (2 equiv), Cs_2CO_3, THF, −78 to 20°C (81%); c) H(O)C-C_6H_4-OH, THF, 20°C (90%); d) $H_2NNMeP(S)Cl_2$, $CHCl_3$, 25°C; e) HO-C_6H_4-PPh_2 (**5**), Cs_2CO_3, THF, 20°C (90%); f) conditions (e) (70%); g) H(O)C-C_6H_4-PPh_2 (**8**), MeOH, 20°C (70%). DMF = dimethylformamide, EDC = *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide, HOBt = 1-hydroxybenzotriazole.

The ability of pyrene-tagged phosphines **9**, **6**-G_0, and **6**-G_1 (Schemes 1 and 2) to interact with graphene layers through π–π stacking was next investigated.[11] The loading was found to decrease as the size of the ligand increased, and loadings of 0.15, 0.1, and 0.03 mmol of pyrene tags per gram of NP were found for **9**, **6**-G_0, and **6**-G_1, respectively (Table 1).[12] Partial desorption of the phosphines from the surface of the NPs was observed when heating the suspension to 60°C, resulting in a decrease of the loading of **6**-G_0 from 0.1 to 0.05 $mmol\,g^{-1}$

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[*] Dr. M. Keller, V. Collière, Dr. A.-M. Caminade, Dr. J.-P. Majoral, Dr. A. Ouali
LCC-CNRS, 205 Route de Narbonne, BP 44099
31077 Toulouse Cedex 4 (France)
Dr. M. Keller, V. Collière, Dr. A.-M. Caminade, Dr. J.-P. Majoral, Dr. A. Ouali
Université de Toulouse; UPS, INPT; LCC
31077 Toulouse (France)
E-mail: caminade@lcc-toulouse.fr
majoral@lcc-toulouse.fr
armelle.ouali@lcc-toulouse.fr
Prof. Dr. O. Reiser
Institut für Organische Chemie, Universität Regensburg
Universitätsstrasse 31, 93053 Regensburg (Germany)

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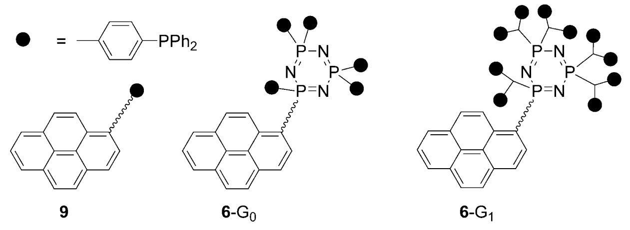


Scheme 2. Structures of monomeric (**9**) and dendritic (**6**-G$_0$ and **6**-G$_1$) phosphine ligands.

Table 1: Binding of **9**, **6**-G$_0$, and **6**-G$_1$ onto NPs through π-stacking, as measured by comparative elemental analysis.[11]

Entry	Pyrene tag	Loading[a]	Phosphine density[b]
1	**9**	0.15	0.15
2	**6**-G$_0$	0.10	0.50
3	**6**-G$_1$	0.03	0.30
4	**6**-G$_0$	0.05[c]	0.25
5	**6**-G$_0$	0.10[d]	0.50

[a] Loading values are given as mmol of pyrene tag per gram of NP. [b] Phosphine density values are given as mmol per gram of NP. [c] Loading of **6**-G$_0$ at 60 °C in THF/H$_2$O (2:5). [d] Loading of **6**-G$_0$ after heating to 60 °C for 14 h and cooling down to 20 °C in THF/H$_2$O (2:5).

(entry 4).[7] However, this desorption is completely reversible, at room temperature the phosphine is again completely absorbed onto the NPs (entry 5). Such reversible desorption from MNPs at 60 °C, bridging homogeneous and heterogeneous processes, can be seen as a major advantage for catalysis compared to traditional covalent grafting, as all functional groups are chemically accessible.[13,14] Moreover, this constitutes the 1st catalytic system grafted by π-interactions in a THF/water mixture, a medium often more suitable for organic reactions than pure water.

Monomeric phosphine **9** and dendrimers **6**-G$_0$ and **6**-G$_1$, which possess five and ten ligands, respectively, on their surface, were tested as ligands for Pd in Suzuki couplings (Figure 1).[15,16] Nanocatalyts based on different organic and inorganic supports have been reported for this versatile and powerful method of C–C bond formation.[2,17,18] To our knowledge, only a few examples of dendronized catalysts supported on MNPs have been reported, and all of them are covalently grafted.[8a,c,d,g]

The coupling of boronic acids with various aryl bromides was performed in the presence of Co/C MNPs, Pd(OAc)$_2$ (0.5 mol %), ligands **9**, **6**-G$_0$, and **6**-G$_1$ (1 phosphine moiety per Pd), and Na$_2$CO$_3$ in a THF/water (2:5) mixture (Figure 1). Good to excellent yields of products **10a–f** (70–98 %) were obtained, even in the cases of electron-rich (R = 4-OMe: **10d**, 4-Me: **10c**) or bulky (R = 2-Me: **10e**) substrates. These conditions are competitive in terms of Pd loading,[18] especially compared to MNP-supported catalysts involving covalently immobilized dendronized Pd complexes, which require 2.4–5 mol % of metal.[8a,d,g] For each substrate, monomeric and dendritic ligands conferred about the same activity to Pd (Figure 1). Interestingly, in reported Suzuki couplings involving dendritic phosphines that are missing the pyrene groups, regardless of whether they are grafted onto MNPs[8a,d] or not,[17a,j] the catalytic activity was found to decrease as the generation increased. The absence of a negative dendritic effect observed here may be due to the presence of the pyrene moiety, which could enhance the performance of the coupling by creating favorable interactions with aryl substrates.[19]

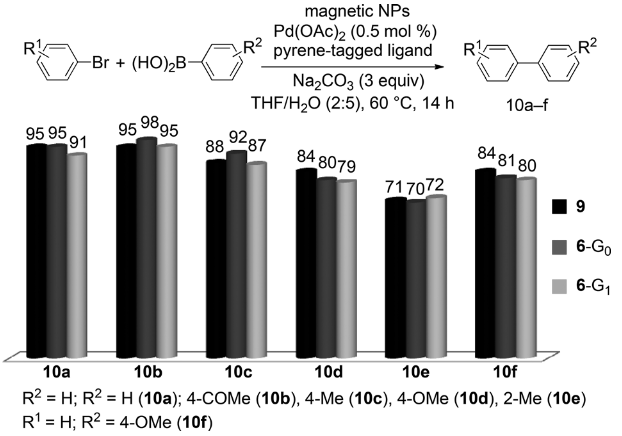


Figure 1. Pd-catalyzed couplings of ArBr and PhB(OH)$_2$ in the presence of pyrene-tagged phosphines and Co/C MNPs. Reaction conditions: Pd(OAc)$_2$ (0.005 mmol), Co/C MNPs, phosphine ligands (0.005 mmol for **9**, 0.001 mmol for **6**-G$_0$, 0.0005 mmol for **6**-G$_1$; Pd/phosphine ratio = 1:1), ArBr (1 mmol), ArB(OH)$_2$ (1.14 mmol), Na$_2$CO$_3$ (3 mmol), THF/H$_2$O (2:5; 7 mL). Bar graph shows yields determined by GC analysis using 1,3-dimethoxybenzene as an internal standard.

Recycling experiments were attempted in the case of ligands **9**, **6**-G$_0$, and **6**-G$_1$ in the preparation of **10a** from PhBr and PhB(OH)$_2$ (Figure 2). Using **9** and **6**-G$_1$, a steady decrease in yield was observed from runs one to four. However, the catalytic system based on **6**-G$_0$ displayed better recycling properties: yields of **10a** remaining unchanged (95 %) over four runs. This may be because **6**-G$_0$ has the highest phosphine density (Table 1) of the three, which may increase the stability of the resulting Pd catalyst and contribute to its robustness. In the absence of pyrene-tagged ligands, the catalyst could not be recovered.

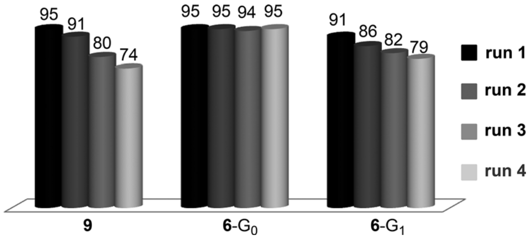


Figure 2. Recycling experiments in the coupling of PhBr and PhB(OH)$_2$ using immobilized catalysts bearing **9**, **6**-G$_0$, or **6**-G$_1$ as the ligand. For experimental conditions, see Figure 1. Bar graph shows yields determined by GC analysis using 1,3-dimethoxybenzene as an internal standard.

HRTEM, scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDX) spectra were recorded on MNP functionalized by Pd complexes involving dendritic phosphine **6**-G$_0$ before (Figure 3 a) and after 5 catalytic cycles (b).[11] In both cases, the MNP were found to be surrounded by gray shells (area 1), which are not visible on

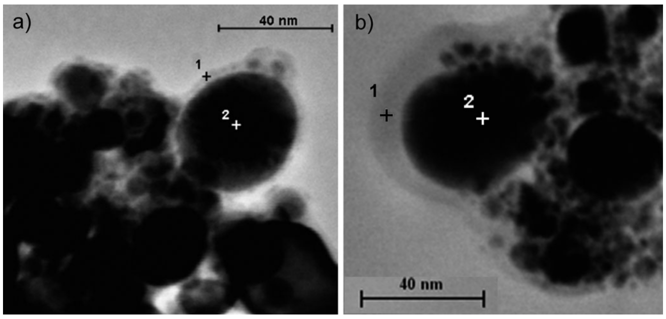
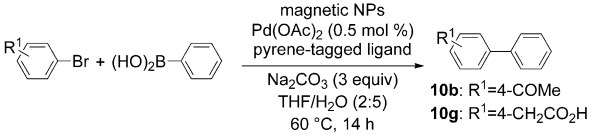
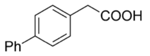


Figure 3. STEM images of Co/C MNPs functionalized by Pd–**6**-G$_0$ complexes before catalysis (a) and after 5 runs (b). Dark regions (areas 2) contain Co (core), whereas the gray shells (areas 1) mainly contain Pd and ligand.

naked Co/C MNPs.[4,7] EDX spectra recorded in both cases show the presence of Pd and ligand in these light regions, whereas the dark areas (area 2) mainly contain Co and correspond to the MNP cores, as expected. These results support effective grafting of the Pd/dendritic phosphine complexes onto the Co/C MNP through π–π-stacking.

Table 2: Recycling of the immobilized catalyst.[a]



Run	Product	Yield [%][b]
1		100 (98)[c]
2–11	**10g**	100
12	**10b**	98 (94)

[a] For reaction conditions, see Figure 1. [b] Yields determined by GC analysis using 1,3-dimethoxybenzene as an internal standard. Yield of isolated products given in parentheses. [c] Contamination levels of the recovered product: crude: 111 ppm Pd, after extraction with CH_2Cl_2: < 5 ppm Pd and < 0.005 ppm Co.

Table 3: Analysis of Pd leaching into crude mixtures during the preparation of **10a** from PhBr and $PhB(OH)_2$.[a]

Run	Pd [ppm]	Yield of **10a** [%]
1	274	95
2	110	95
5	35	95
10	9	95
$Pd(OAc)_2$/**6**-G$_0$ (no MNP)	895	94

[a] The ligand used for all runs was **6**-G$_0$. For reaction conditions, see Figure 1.

The recyclability of the catalyst bearing **6**-G$_0$ was next tested in the preparation of Felbinac **10g**, a commercial non-steroidal anti-inflammatory drug currently used to treat muscle inflammation and arthritis.[20] **10g** could be isolated quantitatively (Table 2, run 1) under conditions competitive to those reported for its preparation, which involve much higher Pd loadings.[21] The catalyst could be reused ten times without loss of activity (runs 2–11). A 12th run was also successful, even when changing the substrate used, with **10b** being obtained quantitatively (overall TON = 2400). Pd leaching was measured by ICP-MS after run 1, and 111 ppm of Pd was detected in the crude (ca. 6% of introduced Pd); extraction with CH_2Cl_2 allowed for the isolation of **10g** with less than 5 ppm of Pd contamination, which meets the requirements of the pharmaceutical industry.[22] No traces of Co were detected. The evolution of Pd leaching over the cycles was also investigated for the synthesis of **10a** (Table 3). A substantial drop in Pd leaching was observed in the crude: 274 ppm (ca. 14% of introduced Pd) after the 1st run, 110 ppm (ca. 6%) after the 2nd, 35 ppm (ca. 2%) after the 5th run and 9 ppm (ca. 0.5%) after the 10th run, while maintaining yields of 95%. These results point to a non-specific binding of Pd outside the ligand; Pd that is removed in the extraction procedures of the first two runs. It is of particular note that significantly reduced Pd leaching was observed with **6**-G$_0$ on MNPs versus the non-recoverable catalyst consisting of only $Pd(OAc)_2$ and **6**-G$_0$: the non-recoverable catalyst system produced three-fold more Pd contamination than its NMP-immobilized analogue.

In summary, we report here the successful combination of several strategies to arrive at novel, recyclable Pd catalysts. Using a magnetic support enables the facile agitation and recovery of the catalyst by simply applying an external magnetic field, which avoids the need for precipitation or filtration steps. Moreover, attaching a dendritic ligand onto the MNP surface allows up to five times higher loading (0.5 $mmol\,g^{-1}$ active sites) than the previously reported direct functionalization of catalysts onto the NP.[7] Finally, immobilization of the ligand by reversible π–π interactions allows the catalysis to proceed in the homogeneous phase at elevated temperatures (60 °C), which was herein demonstrated for the first time in an organic solvent/water mixture rather than in pure water, thus extending the applicability of such catalysts to non-water-soluble substrates. The corresponding Pd complexes were tested in Suzuki couplings and displayed good activity for the preparation of various biaryls. In terms of recyclability, a dendritic effect was observed and the most efficient catalyst (bearing ligand **6**-G$_0$) could be recovered by straightforward magnetic decantation and reused at least 12 times without loss in activity. In terms of catalytic performance, the overall TON and the ease of recovery are two strengths of the reported catalyst over other immobilized systems.[2,17,18] Although the **6**-G$_0$-based catalyst does not completely eliminate Pd leaching into the crude product, Felbinac (**10g**), which was prepared over multiple runs, met the specification limits for metal residues in the pharmaceutical industry (< 5 ppm Pd) after a straightforward extraction with CH_2Cl_2, and without requiring tedious chromatographic purification.[22] The extension of catalyst applications is now underway.

Experimental Section

Catalytic tests and recycling: $Pd(OAc)_2$ (0.005 mmol), Co/C NP (10 mg for **9**, 2 mg for **6**-G$_0$, 1 mg for **6**-G$_1$), and ligand (0.005 mmol of **9**, 0.001 mmol of **6**-G$_0$, 0.0005 mmol of **6**-G$_1$) were added under argon

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to a Radley tube carousel equipped with a magnetic stir bar. THF (2 mL) and H_2O (5 mL) were then added. After 1 h at room temperature, ArBr (1 mmol), $ArB(OH)_2$ (1.14 mmol) and Na_2CO_3 (3 mmol) were introduced. The tube was closed, stirred, and heated at 60 °C for 14 h. After cooling to room temperature, the mixture was sonicated for 30 min at 20 °C. Magnetic decantation with a Nd magnet was then performed and the MNPs were washed 5 times with THF/H_2O (2:5) mixture (5 mL). After concentration of the liquid phase under vacuum, 1,3-dimethoxybenzene (1 mmol, 130 μL), CH_2Cl_2 (15 mL) and H_2O (15 mL) were added. After 2 extractions with CH_2Cl_2, the organic layers were combined, filtered through a plug of Celite and analyzed by GC or isolated by column chromatography. The solid was directly used for a new catalytic run. THF (2 mL), H_2O (5 mL), ArBr (1 mmol), $ArB(OH)_2$ (1.14 mmol) and Na_2CO_3 (3 mmol) were introduced under argon. The flask was closed, stirred, and heated at 60 °C for 14 h.

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